UNIVERSITY OF PENNSYLVANIA

THE THERMODYNAMIC PROPERTIES OF SOLUTIONS OF ONE-TENTH MOLAL HYDROCHLORIC ACID, CONTAINING CALCIUM, STRONTIUM AND BARIUM CHLORIDES

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NORMAN JODON BRUMBAUGH

A THESIS

PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY

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The author desires to express his appreciation to Dr. Herbert S. Harned, who suggested the general plan of this investigation and from whom valuable assistance and direction were frequently received.

THE THERMODYNAMIC PROPERTIES OF SOLUTIONS OF 0.1 MOLAL HYDROCHLORIC ACID CONTAINING CALCIUM, STRONTIUM AND BARIUM CHLORIDES.

In several recent contributions, Harned (Jour. Amer. Chem. Soc. 37, 2460 (1915); 38, 1986 (1916); 43, 1808 (1920) from measurements of cells of the type

$$H_2|MeCl\ (c)\ in\ HCl\ (0.1)|\ HgCl\ |Hg$$
$$and\ H_2|MeCl\ (c)\ in\ HCl\ (0.1)|Sat.KCl|HgCl|Hg$$

where Me represents potassium, sodium, or lithium, has attempted to compute the independent hydrogen and chlorine ion activities of these solutions. In all these cells the concentration of the acid has been kept constant and the salt varied. Loomis, Essex and Meacham (Jour. Amer. Chem. Soc. 39, 1133 (1917) and Ming Chow (ibid. 42,488 (1920), have also measured cells of the same type containing hydrochloric acid and potassium chloride, but in their measurements the total chlorine ion concentration was kept constant.

In the present investigation accurate measurements of the same types of cells have been made, employing barium, strontium and calcium chlorides in 0.1 M hydrochloric acid. The exact calculation of the individual activity coefficients of the ions in concentrated solutions is a problem accompanied with great difficulties owing to liquid junction potentials which cannot be accurately calculated. At the present time, the only other method of value, besides calculations which are inexact, is to eliminate as far as possible the liquid junction potential by the use of a saturated potassium chloride solution. From previous results obtained by Harned (loc. cit.) there is considerable evidence that the difference in liquid junction potential between

$$HCl\ (0.1)|Sat.\ KCl$$
$$and\ HCl\ (0.1)\ +MeCl\ \ |Sat.\ KCl$$

if present at all, is very small, probably amounting to less than a millivolt when the MeCl is as concentrated as 2M. Although this error due to liquid junction is appreciable, and the calculations cannot be regarded as exact, it is thought that further experimental work of this nature is of very great value, particularly since no other method has yet been found which can approach it in accuracy.

1. General Theory.

If a process is carried out reversibly, the maximum work is independent of the path. Hence, if the system passes from a state I to a state II, the maximum work may be regarded as the difference in two quantities A_1 and A_2. Thus,

Maximum work $= A_1 - A_2 = -(A_2 - A_1) = (-\Delta A)$

Now, take for example, the voltaic cell

$$Zn \mid Zn^{++} \parallel H^+ \mid H_2$$

and let the process

$$Zn + 2H^+ = Zn^{++} + H_2$$

take place reversibly at constant pressure producing the electrical work W. W is not the quantity $(-\Delta A)$ for besides W there will be the work $P\Delta V$ done by the production of 1 mol. of hydrogen. Hence,

$$W = (-\Delta A) - P\Delta V \qquad (1)$$

Let $F = A + \Sigma pV$

and $\Delta F = \Delta A + \Sigma p\Delta V \qquad (2)$

ΔF will be the increase in free energy of the system. In the above cell let nEF be the electrical work. Then, the total maximum work will be $(-\Delta A)$ and

$$(-\Delta A) = nEF + p\Delta V \qquad (3)$$

or from (2) and (3)

$$nEF = (-\Delta A) - p\Delta V = (-\Delta F)^*$$

*(See Lewis—Jour. Amer. Chem. Soc. 35, 1 (1913)

Thus, the electrical work at constant pressure and temperature of a reversible cell is equal to the free energy decrease. In order to calculate ΔH, the increase in heat content function, from measurements of ΔF, use will be made of the fundamental thermodynamic formula

$$\Delta H = \Delta F - Td\left(\frac{\Delta F}{dT}\right) \qquad (4)$$

The activity can be defined by the equation

$$\bar{F} = RT \ln a + i \qquad (5)$$

where $\bar{F}$ is the partial molal free energy, i a constant, R the gas constant and T the absolute temperature.

Thus, the free energies of an ion species in two states are related by

$$\Delta F = \bar{F}_2 - \bar{F}_1 = RT \ln \frac{a_2}{a_1} \qquad (6)$$

(6) will be the exact formula for the free energy change of a concentration cell. Consider the general reaction

$$aA + bB + \ldots\ldots = dD + eE \ldots\ldots$$

Let it take place electrically. Then it is easily proved (Lewis—loc. cit.) that

$$(-\Delta F) = nEF = -RT \ln \frac{a_D^d \quad a_E^e}{a_A^a \quad a_B^b} \qquad (7)$$

Two types of cells will be considered in the present investigation:

Type I H_2 | $MeCl_2$ (c) in HCl (0.1) | HgCl | Hg

Type II H_2 | $MeCl_2$ (c) in HCl (0.1) | Sat.KCl | HgCl | Hg

The electromotive forces of the above cells will be denoted by E(1), and E(2) respectively. Also let $E_o(1)$ equal E(1) when $c = o$; $E_o(2)$ equal E(2) when $c = o$.

2 E(1)F will be the free energy decrease $(-\Delta F)$ of the cell reaction.

$$H_2 + 2\,HgCl = 2\,Hg + 2\,HCl\ (c)$$

in the presence of HCl (0.1M) and the acid-salt mixtures. Then

$$F[E_o(1) - E(1)] = (-\Delta F)_1 = RT \ln \frac{a_{H(s)} \quad a_{(Cl+0.1)}}{a_{H(0.1)} \quad a_{Cl(0.1}}$$

where $(-\Delta F)_1$ is the decrease in free energy of transfer of two mols of hydrochloric acid from ($MeCl_2$ (c) + HCl (0.1) to HCl (0.1). ($a_{H(s)}$) refers to the activity of the hydrogen ion in the acid-salt mixtures.)

Further $$F[E_o(2) - E(2)] = (-\Delta F)_2 = RT \ln \frac{a_{H(s)}}{a_{H(0.1)}}$$

if, in the latter case, the potassium chloride solution eliminates the liquid junction difficulties.

A further quantity which is often used is the activity coefficient which for a single ion is defined by $\frac{a}{c}$ where c is the molal concentration of the ion.

2. Experimental.

a. *Materials.*

The various chemicals used in making the cells were carefully tested as to their purity and most of the materials were prepared for this particular investigation from analyzed chemicals. The aim sought was to avoid error in the electromotive force measurements from possible contaminating impurities in the stock materials.

The mercury used was distilled three times under reduced pressure. During the distillation a stream of air was passed through the mercury in the flask in order that all traces of zinc and cadmium might be oxidized and thereby separated from the vaporized mercury. This purified mercury was used in the calomel electrode chamber of all the cells. Also a

portion of it was treated with a limited amount of nitric acid which had been previously redistilled over solid potassium permanganate. From a boiling solution of the mercurous nitrate thus formed, the calomel for the cells was precipitated by the addition of redistilled hydrochloric acid. The precipitated calomel was washed until all traces of hydrochloric acid had disappeared, about forty times. The last two or three washings were made with redistilled water.

All water used in making up solutions of the electrolytes had been redistilled from an alkaline potassium permanganate solution through a block tin condenser.

The barium chloride was prepared from commercial barium chloride by three successive crystallizations, the last one being made from the conductivity water. The salt thus obtained was analyzed.

A stock solution of strontium chloride of almost the maximum saturation at 18° was made from a special grade of analyzed chemicals. The purity of the strontium chloride in this concentrated solution was tested by precipitating the chloride as silver chloride, and calculating the chloride found in terms of the strontium content. The chloride analysis was checked by an independent analysis of samples of the same solution by precipitation of strontium sulphate from an aqueous alcoholic solution and again calculating the resulting strontium sulphate as strontium. The mean of the chloride analyses gave a strontium content of 33.820%, and that of the sulphate analysis 33.740%, an actual difference of .08%, or a precentage difference of a little over two-tenths of one per cent. The strontium chloride was further tested spectroscopically and found to be free of barium; even sodium was present apparently in minute quantity.

Analyzed anhydrous calcium chloride was added to conductivity water in excess. The solution was filtered, and to it, was added a slight excess of the redistilled hydrochloric acid sufficient to overcome the alkaline reaction of the original solution. This excess of hydrochloric acid was eliminated by adding precipitated calcium carbonate to the solution and passing air through the boiling solution to remove carbon dioxide gas. The solution was then neutral. Three samples of the calcium chloride solution thus prepared were treated with silver nitrate and from the weights of the silver chloride, the calcium content was calculated, giving 4.163, 4.162 and 4.161 per cent, an average value of 4.162 per cent. Three other samples of the same solution were evaporated to dryness with dilute sulphuric acid and the calcium content was determined from the weights of the calcium sulphate, the values being 4.152, 4.166 and 4.145 per cent, giving an average value of 4.154 per cent. The difference between this last value and the

average value for the calcium content by the chloride method is 0.008%, or in terms of the mean calcium content, 4.158, the difference is a little less than two-tenths of one per cent.

b. *Apparatus.*

Measurements of this type have been made by numerous investigations (Acree Am. Chem. J. 46, 632, 1911; Harned, J. A. C. S. 37, 2460, 1915; Ellis, J. A. C. S. 38, 737, 1916; Lewis, Brighton & Sebastian, J. A. C. S. 39, 2245, 1917), but the cells employed here differed in some respects from any previously described. One type of cell was employed for the measurement of the combination

$$H_2 \mid MeCl_2\ (c) \text{ in } HCl\ (0.1) \mid HgCl \mid Hg$$

It was an H shaped cell and is shown in Fig. 1.

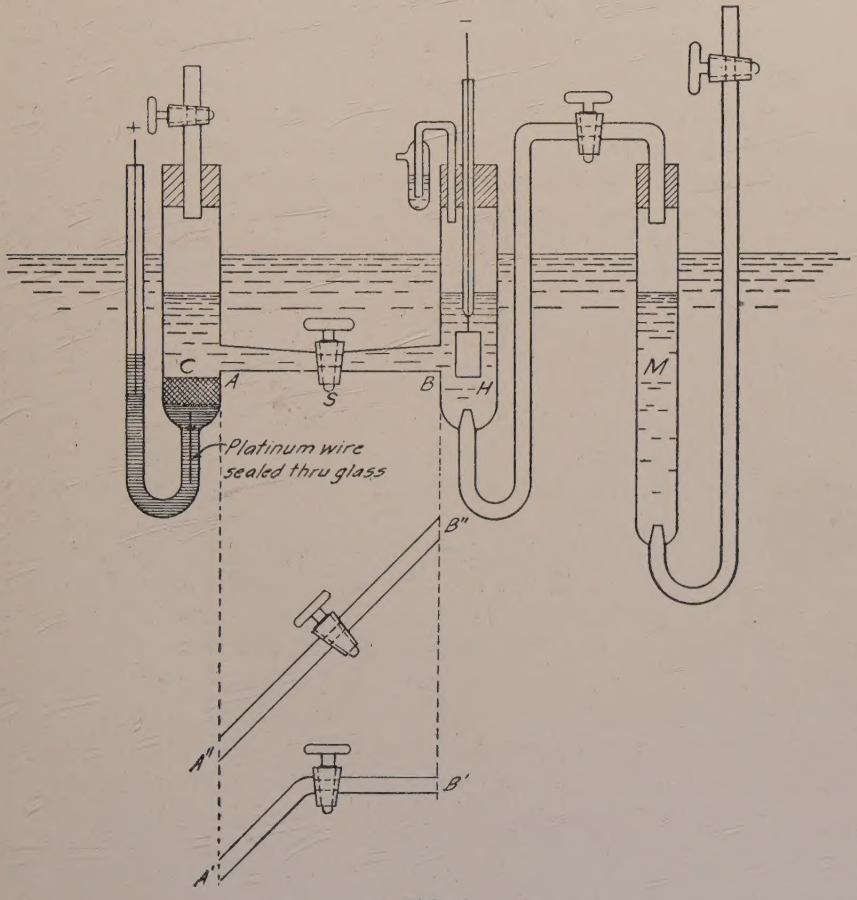

FIG. 1

The side marked C is the calomel electrode. In the first cells contact on the calomel electrode side was made through a glass tube fixed in a one-hole rubber stopper in the end of which tube was sealed a platinum wire similar to the arrangement shown in the calomel side, C, of Fig. 2. It sometimes happened, however, that when the rubber stopper holding the glass tubing was inserted into the calomel limb of the cell, air pressure was produced in the calomel chamber above the solution. When the stopcock S was subsequently opened for a measurement a certain amount of calomel, lodged between the points A and S, would be suddenly carried through to the hydrogen electrode side. The lead wires for the calomel electrode were therefore thrust into mercury in the small side tube shown to the left of C which, in turn, was in contact with the calomel electrode through a platinum wire fused into the bottom of the cell. The stopcock shown above C was always kept open until the rubber stopper in which the former was fixed had been securely inserted into the top of the tube. By following this procedure no calomel was forced into the hydrogen compartment.

In the first cells used the connecting tube of the cell AB, Fig. 1, was a piece of straight side glass tubing. Frequently, however, air bubbles collected near the stopcock S and very persistently remained there. By replacing the straight side tubing with a tubing flared at either side of the stopcock S, as shown by AB, Fig. 1, any bubbles which were present when the cell was set up were very easily removed.

As mentioned later, it was customary to shake the cell until its electromotive force had attained a constant value. This shaking invariably caused some calomel to lodge even in the flared tube between the points A and S as a result of which, if the stopcock were opened for some time, a certain small amount of calomel might be carried into the hydrogen electrode chamber. In order to eliminate this, a connecting tube of the shape indicated by A′ B′ was tried. A certain amount of calomel, it was observed, still lodged near the stopcock just above the elbow of the tube. Moreover, at the same point in the tube A′B′ a bubble would collect which was difficult to dislodge. Finally, therefore, a connecting tube of the type shown at A″B″ was used. By pouring the electrolyte into the tube first until the side SB″ was completely filled, and then adding the calomel, the presence of air bubbles near the stopcock was entirely avoided. The calomel here used had previously been equiliberated at 25° with a solution of the particular chloride of a definite concentration for several days. This arrangement of the connecting tube A″B″ at an angle of about 45° to the limbs of the cell had the marked advantage that no calomel would lodge near the stopcock, for after each shaking it would roll to the bottom of the calomel electrode chamber.

The hydrogen electrode was kept always completely immersed in the electrolyte and placed in such a position that the hydrogen bubbles coming from the equiliberating chamber M would be divided by the platinum foil. The hydrogen electrode chamber was provided with a trap T permanently inserted in the rubber stopper which closed the tube. By having the end of the small escape tube of the trap under the surface of the electrolyte in the bowl of the trap, the space above the surface of the liquid in the hydrogen electrode chamber was kept filled with hydrogen.

The hydrogen was first passed through a solution of the electrolyte in the equiliberating tube M, thereby becoming saturated before coming into contact with the solution in the hydrogen electrode chamber, and thus preventing any evaporation in the chamber. It has been determined that equiliberating tubes of the above type (M in Figs. 1 & 2) are satisfactory for saturating the hydrogen.

After each measurement the hydrogen electrode was removed, any possibly adhering calomel (indicated by a gray color instead of the intense black of the platinum sponge) was dissolved by immersing the electrode in nitric acid. After rinsing with distilled water the electrode was recoated by making it the cathode in a chlorplatinic acid solution, from twenty to forty-five minutes, the current density being from 20 to 50 milli-amperes.

$$H_2 \mid MeCl_2\ (c) \text{ in HCl } (0.1) \mid KCl(\text{Sat.}) \mid HgCl \mid Hg$$

Fig. 2 represents the potassium chloride cell.

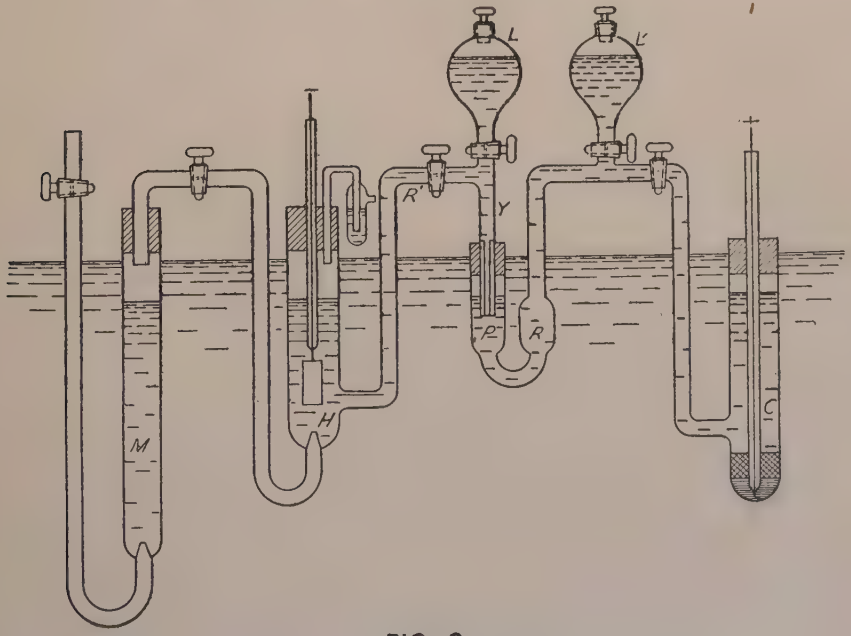

FIG. 2

Calomel previously equiliberated for several days with a solution of potassium chloride saturated at 25° was poured into the calomel chamber C along with the mercury. The bridge RR was then carefully filled with the same potassium chloride solution, as well as the cup P. At the bottom of the cup a few crystals of potassium chloride were always present. The bulb L′ was likewise filled with the solution. The equiliberating tube M, the hydrogen electrode chamber H, the bridge R′, as well as the bulb L, were all filled with a solution of the particular electrolyte being measured, that is with $MeCl_2$ (*c*) in HCl (0.1). This electrolyte filled the capillary tubing Y the end of which dipped into the saturated potassium chloride solution in the cup P when a measurement was being made.

When no measurements were being taken, a cup, really a short test tube of heavy glass fitted over the rubber stopper on the end of the capillary Y where previously the cup P had been. By means of this device the saturated potassium chloride half of the cell, C RP, would be successively attached to any number of half cells, YR′HM. After each measurement the solution from the reservoir bulb L was run through the capillary and the potassium chloride carefully removed from the outside surface of the capillary tubing by bibulous paper. Similarly, the potassium chloride solution was renewed by opening the stopcock below the bulb.

The hydrogen was generated electrolytically by passing the current through a 10% solution of sodium hydroxide. A current of about two amperes was used. A 20% sodium hydroxide solution was first tried but this attacked the electrodes. Even with a 10% solution it was found that copper in contact anywhere with the sodium hydroxide solution was attacked. Finally a platinum anode suspended by a nickel wire and a nickel cathode held in place by a wire of the same material were used in the generator. A cell thus built seemed to be able to supply hydrogen continuously and for an indefinitely long time. Finally, the glass vessels which contained the alkali solution were attacked to some extent. In order to maintain a constantly uniform gas pressure, each cell was provided with its own hydrogen generator. During the greater part of the investigation three cells were being measured simultaneously; for a short time four cells were set up.

To prevent any admixture of the hydrogen with oxygen the tube in which the anode was suspended extended almost to the bottom of the vessel containing the electrolyte. The electrolyte was forced up into this same tube by the back pressure of the generated hydrogen. The level in this tube was regulated by the stopcock attached to the tube M (Figs. 1 & 2), and was maintained at such a height that the hydrogen bubbled regularly and continuously through the hydrogen electrode compartment, H. Be-

tween the hydrogen generator and the cell there was placed first in the hydrogen line a Dreschel wash bottle containing concentrated sulphuric acid. The hydrogen was then led through a tower containing sticks of fused sodium hydroxide, after which it entered the equiliberating vessel M The electromotive force of the cells was measured on a Wolff potentiometer having a total resistance of 15,000 ohms. A null point was obtained by balancing the cell against two large Weston cells (Hulett—Physical Review—1909) in series. Before and after each measurement the latter were compared with a standard Weston cell. The latter in turn was occasionally compared with a new Weston certified by the Bureau of Standards in 1921.

Immediately before taking a set of readings the stopcocks S, Fig. 1, on all the cells were opened, the large Hulett design Weston compared with the standard, after which the cells were read in rapid succession. Each cell had its own lead wires to a three way cup switch placed beside the potentiometer. Finally the large working cells were rechecked and the stop cocks closed.

The temperature of the bath was controlled to within $+.05°$ by means of a very large vessel filled with toluene whose volume, changing with the temperature, moved a thin mercury column in immediate contact with the toluene. The mercury made electrical contact with a platinum wire and thereby opened and closed the electric heating circuit.

c. *Measurements.*

All of the electrolytic solutions were made up on the basis of a fractional or multiple part of a mole per 1000 grams of water. The amounts of the constituents of each solution were determined by weight; in no single instance were volumetric methods employed. Temperature coefficients were thereby eliminated. The strengths of the stock solutions of hydrochloric acid, calcium chloride and strontium chloride were determined by precipitation of silver chloride.

For weighing substances up to about 70 grams, a balance with a sensitiveness of two ten thousandths of a gram per division of pointer scale was used; for larger quantities a beam balance with a sensitiveness of approximately two one hundredths of a gram per scale division was available. The stock solution of redistilled hydrochloric acid analyzed for its acid content at the beginning of the investigation had a mean value of 7.3237% for four samples, with a maximum deviation from the mean for any one sample of 0.0057%, and a maximum difference for any two samples of 0.010%. Because the hydrochloric acid present in the cells was the most

important constituent of the electrolyte, the stock solution was reanalyzed at the end of the investigation and found to have an acid content of 7.3335% with a maximum difference of 0.0082% and a maximum deviation of +.0051%. The change had been negligible. The values of several cells were checked with solutions having the slightly different acid factor, and found to be practically unchanged. Two samples of the calcium chloride solution gave a mean value of 31.847% content with a difference of 0.005%, and two analyses of the strontium chloride solution indicated that 19.284% of the compound was present. In the latter analysis the difference was 0.024%. It might be noted that in order to secure concordant results of these almost saturated salt solutions, it was found necessary to wash the precipitated silver chloride at least ten times with acidulated water.

From the determination of the concentration as described above, the molal content of each solution was obtained by dividing the strength of the solution expressed in per cent by the molecular weight of the particular salt. Since it was necessary to know the weight of the solution containing one molecular weight of the salt the molar strength as found above was divided into the per cent of water present with the salt. This latter number was obviously obtained by subtracting the salt concentration expressed in per cent from one hundred. The result multiplied by a hundred and added to the gram molecular weight of the particular chloride gave the total weight of solution per mol. of salt. For fractional molar solutions, proportional parts of this number were taken.

The amount of water to be added was easily found from the above calculation. The water present with the one-tenth molal hydrochloric acid also decreased by its weight the water necessary to make the one thousand grams present with the salt. In the barium chloride solutions fractional parts of the two molecules of water of crystallization were regarded as a part of the water of dilution.

The calomel which was to be used for the cells was shaken at least eight times with separate portions of the particular solution after which it was allowed to stand in the thermostatic bath at 25° for some hours before using. A cell did not attain its maximum voltage until the hydrogen electrode had been exposed to the stream of hydrogen for about six hours. Before a reading was taken the stopcock S, Fig. 1, was opened, then closed, and the cell shaken. After the calomel had settled the reading of the electromotive force of the cell was checked. This procedure was continued until the cell had acquired a relatively constant voltage. In the case of the concentrated potassium chloride cells, Fig. 2, the calomel electrode side of which was attached in turn to each salt-acid hydrogen electrode half as

previously mentioned, this shaking process was discontinued after a constant and correct value for the combination

$$H_2 \mid HCl\ (0.1) \mid KCl\ (Sat.) \mid HgCl \mid Hg$$

had been secured. The value regarded as correct was that obtained by Fales and Vosburgh (loc. cit.) namely 0.3103. The value here found as a result of fifty checked and separate groups of readings was 0.3100, which is practically within the limit of error as given by the investigators referred to above. The HCl (0.1) side of a cell was kept in the bath and used as a check on the electromotive force values of the salt-acid cells.

After the double cell (Fig. 1) had attained constant value at 25° the temperature of the thermostatic bath was changed to either 18° or 30°, the stopcock opened and the voltage read. The cell was then shaken, and, if a change in value occurred, repeatedly shaken until constancy was obtained. Then the bath was brought back to its initial temperature and the cell again tested. The differences in voltage between the averages of the values thus obtained were used for the determination of the temperature coefficients. (Table III.)

The mean values for the electromotive force readings of the double cells are given in Table I.

TABLE I.

25° VALUES E. M. F. DOUBLE CELLS

c	$BaCl_2$	$SrCl_2$	$CaCl_2$
0.00	0.39898	0.39898	0.39898
0.10	0.37530	0.37500	0.37462
0.20	0.36337	0.36318	0.36305
0.30	0.35503	0.35449	0.35326
0.50	0.34155	0.34031	0.33986
0.75	0.32786	0.32630	0.32529
1.00	0.31678	0.31471	0.31176
1.3	0.30358		0.31280

The object of the investigation was not primarily to establish the electromotive force value of any one particular strength of a single salt but to determine the relative values for the different strengths of all three salts. Therefore, at first, cells of different solution strengths of the same salt were measured and the results plotted.

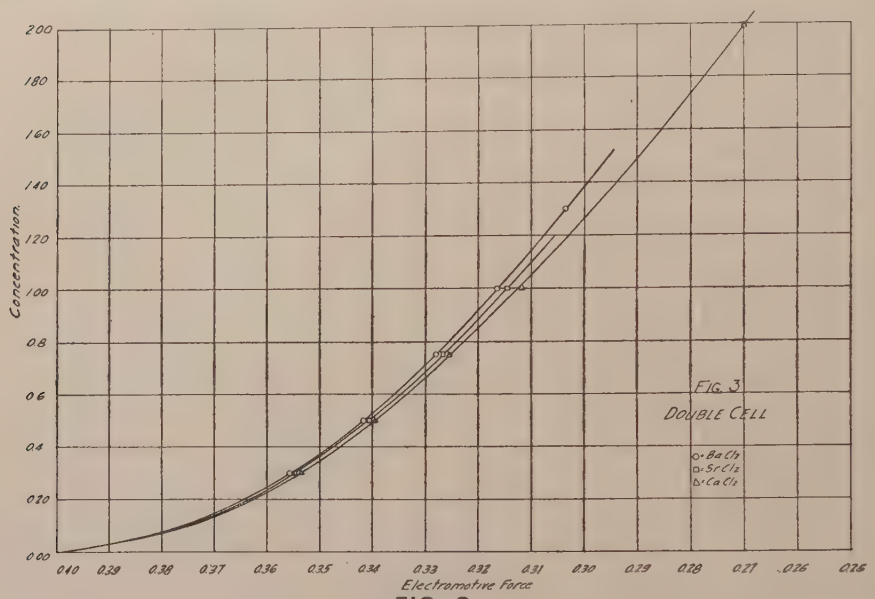

FIG. 3

Where the values were obviously incorrect in comparison with neighboring points on the graph of the same salt or of the other two salts, new cells of that strength were placed in the bath and kept there until the value of the electromotive force was established beyond doubt. Thus it followed that certain cells were read but a few times while the mean value for others was the result of numerous sets of readings. The value of the 1.M strontium chloride cell is the mean of more than fifty readings, the 1.M calcium chloride of over twenty readings and that of the three-fourths strontium chloride of some forty readings; no cell was read less than four times at each temperature.

It is thus evident that the control of the work depended upon the graphs, Figs. 3 & 4. While some of the values depicted upon the graphs are the results of less than a dozen readings, it should be noted that neighboring points on the same smooth line are established by many readings. These latter values may therefore be regarded as control points or control values. One cell only of each kind was set up in the bath at any one time. The mean values in Table I are therefore dependent upon readings taken on different days. It should be added that all the cells except those noted below were read over a period of at least three days and frequently a week. The values for the one-tenth molal strength of the double cells are the only ones which depend upon one day's readings. It is apparent that the values obtained represent readings which were made at different times over a considerable period and should therefore be easily reproducible.

The variation in the e. m. f. values of ten of the cells amounted to approximately one-tenth of a millivolt. In six, the variation ranged from two-tenths to five-tenths. In the case of the three-tenths barium chloride and of seventy-five hundredths calcium chloride the values given in Table I are each the result of two sets of independent readings which varied by one millivolt but these values are the only ones of the kind in the table. It is believed that the cells were reproducible to within ± 0.2 of a millivolt.

The values found for the temperature coefficients are given in Table III.

TABLE III.

$\frac{\Delta E}{\Delta T}$ DOUBLE CELLS

	$BaCl_2$		$SrCl_2$		$CaCl_2$	
c	25°–18°	30–25	25–18	30–25	25–18	30–25
.1	+0.000125	+0.000098	+0.000108	+0.000083	+0.000098	+0.000070
.2	+0.000092	+0.000069	+0.000062	+0.000044	+0.000049	+0.000019
.3	+0.000064	+0.000044	+0.000027	+0.000012	+0.000010	−0.000020
.5	+0.000018	+0.000000	−0.000025	−0.000040	+0.000053	−0.000082
.75	−0.000028	−0.000046	−0.000076	−0.000095	+0.000117	−0.000145
1.00	−0.000070	−0.000089	−0.000120	−0.000146	+0.000172	−0.000200
1.3	−0.000120	−0.000140				

These values were obtained by plotting the differences in voltage at 18°, 25° and 30° and continuing the measurements until acceptably constant results were obtained. In certain cells, notably the calcium cells, the variation was remarkably small, in fact so little as 0.003 millivolt. In other cells the variation was larger. It is believed that the temperature coefficients are reproducible to within $\pm$ 0.005 millivolt.

TABLE II.

E. M. F'S. FOR CON. KCl CELLS—25°

c	$BaCl_2$	$SrCl_2$	$CaCl_2$
0.1	0.00140	0.00160	0.00194
0.2	0.00301	0.00337	0.00390
0.3	0.00480	0.00530	0.00599
0.5	0.00882	0.00959	0.01041
0.75	0.01432	0.01531	0.01641
1.00	0.01989	0.02141	0.02310
1.30	0.02658		

The voltage values for the half cells (Fig. 2), subtracted from the HCl—no salt value mentioned above (0.3100), are given in Table II, and are plotted in Fig. 4.

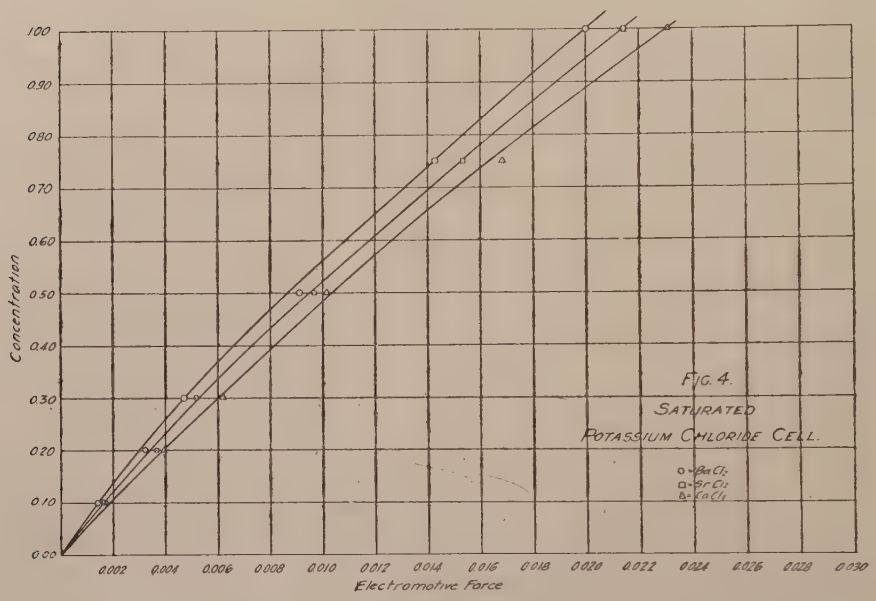

FIG. 4

The electromotive force readings were corrected for partial hydrogen pressure by direct reading of the correction from graphs showing variation of voltage with barometric pressure for each one of the three temperatures at which measurements were made. The values for the e. m. f. indicated on the chart were derived from the expression (Harned—loc. cit.)

$$E = \frac{RT}{2F} \ln \frac{760}{P_p - P_{H_2O}}$$

It should be stated that considerably more difficulty was experienced in measuring the concentrated electrolytes than with the more dilute, both in establishing electromotive force values and in determining temperature coefficients. It is here suggested that this difficulty was possibly caused by an appreciable solubility of the calomel electrode in the concentrated solutions of the salts under consideration.

III. (a) THE FREE ENERGY AND HEAT CONTENT INCREMENTS OF THE CELL REACTION.

The decrease in free energy resulting from the reaction in the cell of

$$2\,HgCl + H_2 = 2\,Hg + 2\,HCl\ (0.1M)$$

has been computed from the values for the electromotive force given in table IV for 18°, 25° and 30° by multiplying each value there given by 2 x 96500.

TABLE IV.

c	E_{18}	E_{25}	E_{30}
$BaCl_2$			
0.00	0.39785	0.39898	0.39963
0.1	0.37443	0.37530	0.37579
0.2	0.36273	0.36337	0.36372
0.3	0.35458	0.35503	0.35525
0.5	0.34142	0.34155	0.34155
0.75	0.32806	0.32786	0.32762
1.00	0.31727	0.31678	0.31633
1.3	0.30442	0.30358	0.30288
$SrCl_2$			
0.1	0.37424	0.37500	0.37544
0.2	0.36265	0.36318	0.36340
0.3	0.35429	0.35449	0.35455
0.5	0.34049	0.34031	0.34011
0.75	0.32683	0.32630	0.32581
1.00	0.31555	0.31471	0.31398
$CaCl_2$			
0.1	0.37393	0.37462	0.37497
0.2	0.36271	0.36305	0.36315
0.3	0.35319	0.35326	0.35316
0.5	0.34022	0.33986	0.33929
0.75	0.32612	0.32529	0.32456
1.00	0.31296	0.31176	0.31076

The decrease in free energy thus determined for 18, 25 and 30 degrees is given for each concentration of the salts in Table V, columns 2, 3 and 4.

TABLE V.

c	$(-\Delta F)_{18}$	$(-\Delta F)_{25}$	$(-\Delta F)_{30}$	$\frac{\Delta F}{\Delta T}$	$(-\Delta H)_{25}$
$BaCl_2$					
0.00	76785.	77003.	77129.	+29.0	68361.
0.10	72265.	72433.	72527.	+21.00	66175.
0.20	70007.	70130.	70198.	+14.50	65809.
0.30	68434.	68521.	68563.	+ 9.50	65690.
0.50	65894.	65919.	65919.	+ 1.30	65474.
0.75	63316.	63277.	63231.	− 7.00	65363.
1.00	61233.	61139.	61052.	−15.50	65758.
1.3	58753.	58591.	58456.	−25.00	66041.
$SrCl_2$					
0.1	72228.	72375.	72460.	+19.00	66713.
0.2	69991.	70094.	70136.	+10.80	66935.
0.3	68378.	68417.	68428.	+ 4.03	67225.
0.5	65715.	65680.	65641.	− 6.40	67557.
0.75	63078.	62976.	62881.	−17.50	68191.
1.00	60901.	60739.	60598.	−27.50	68934.
$CaCl_2$					
0.1	72168.	72302.	72369.	+15.00	67832.
0.2	70003.	70069.	70088.	+ 5.02	68579.
0.3	68166.	68179.	68160.	− 2.30	68864.
0.5	65662.	65593.	65483.	−14.00	69646.
0.75	62941.	62781.	62640.	−25.50	70386.
1.00	60401.	60170.	59977.	−35.50	70749.

In determining the heat content function $(-\Delta H)$ column five, table V, the expression

$$(-\Delta H) = (-\Delta F) - Td\frac{(-\Delta F)}{dT}$$

was used. But it was found at least to be impracticable if not impossible to express $\Delta F)$ as a function of T and subsequently to differentiate the equivalent expression

$$\frac{d(\Delta F)}{dt} = -\frac{\Delta H}{T^2}$$

and from this differentiated expression to calculate the numerical value of $(-\Delta H)$. For it was evident that $\Delta F = f(T)$ varied markedly for various concentrations of the three different salts. The values for

$$Td\left\{\frac{-\Delta F}{dT}\right\}$$

were therefore determined by a graphic method. The values of the free energy decreases as given in columns 2, 3 and 4, Table V, were plotted against their respective temperatures and a smooth curve was drawn through the three points thus determined. The scales used for plotting differed for the various groups of free energy values. In general, when the variation of free energy with the temperature was slight, a large scale was employed. Thus, in the case of five-tenths barium chloride and of three-tenths calcium chloride a scale of five-tenths of a centimeter per joule and of 2 centimeters per degree was used. For most of the concentrations, however, a scale of one-tenth or of one-fifth of a centimeter per joule and of 1 centimeter per degree was found to be satisfactory. The increase or decrease in energy for one-half of a degree on either side of the 25° value was scaled off on the curve. The values thus obtained are given in column five, Table V.

In order to check the values for

$$d\left(\frac{-\Delta F}{dT}\right)$$

column five, Table V, each one of these values was plotted against the corresponding salt concentration. All of these points should exactly determine a curve which should be perfectly smooth and give no evidence of discontinuities. All points were directly on such curves except those for five-tenths barium chloride and three-tenths calcium chloride; values for these concentrations given in column 5, Table V, were scaled from the last mentioned curves. These values did not lie directly on their respective curves because it is evident from their free energy values for 18°, 25° and 30°, Table V, that each has a maximum free energy value between 18° and 25° which value could not be determined unless the temperature coefficients for that particular temperature were known.

By multiplying each one of these values for $\frac{\Delta F}{\Delta T}$ by the value of T (=298°) and subtracting the result from the corresponding value for the free energy at 25°, Table V, columns 2, 3 and 4, the values in joules of the change in heat content function are determined. They are tabulated in column five, Table V.

b. THE FREE ENERGY AND HEAT CONTENT DECREASE OF TRANSFER OF 2 MOLS. OF HC1 FROM $MeCl_2$ (0) IN HC1 (0.1M) to HCL (0.1M).

The free energy and heat content function of the transfer of two gram ions of hydrogen and chlorine are given in Table VI.

TABLE VI.

c	18°	25°	30°	$(-\Delta H)_{25}$
$BaCl_2$				
0.1	4520.	4570.	4602.	2186.
0.2	6778.	6873.	6931.	2552.
0.3	8351.	8482.	8566.	2671.
0.5	10891.	11084.	11210.	2887.
0.75	13469.	13726.	13898.	2998.
1.00	15552.	15864.	16077.	2603.
1.3	18032.	18402.	18673.	2320.
$SrCl_2$				
0.1	4557.	4628.	4669.	1648.
0.2	6794.	6909.	6993.	1426.
0.3	8407.	8586.	8701.	1136.
0.5	11070.	11323.	11488.	804.
0.75	13707.	14027.	14248.	170.
1.00	15884.	16264.	16531.	−573.
$CaCl_2$				
0.1	4617.	4701.	4763.	529.
0.2	6782.	6934.	7041.	−218.
0.3	8619.	8824.	8969.	−503.
0.5	10923.	11410.	11646.	−1285.
0.75	13844.	14212.	14489.	−2025.
1.00	16384.	16833.	17152.	−2388.

They were obtained by subtracting the values for the decrease in free energy for each salt concentration (Table V) from the value for the free energy given at the top of Table V, at salt concentration 0.00. In a similar manner the heat content function values were obtained from Table V and are given for 25° in the last column of Table VI.

c. INDEPENDENT ACTIVITIES OF IONS.

MacInnes (loc. cit.) first clearly pointed out that in solutions of different electrolytes having a common ion, the latter may have the same activity independent of the accompanying ions. In particular the ratio of

the activity of the chloride ion in a given concentration of the latter to a constant concentration of the same ion should be identical for barium, strontium and calcium chlorides. The data obtained in this investigation affords further proof of this theory. (Harned, J. A. C. S., 43, 1814, 1920.)

Mathematically the above mentioned ratio may be obtained by using equations (8) and (9) of this paper. If (9) is subtracted from (8) we have

$$F[E_o(1)-E(1)]-F[E_o(2)-E(2)]=RT\ln\frac{a_{H(s)}\ a_{Cl(C+0.1)}}{a_{H(0.1)}\ a_{C(0.1)}}-RT\ln\frac{a_{H(s)}}{a_{H(0.1)}}$$

that is,

$$[E_o(1)-E(1)]-[E_o(2)-E(2)]=\frac{RT}{F}\ln\frac{a_{H(s)}}{a_{H(0.1)}}+\ln\frac{a_{Cl(C+0.1)}}{a_{Cl(0.1)}}-\ln\frac{a_{H(s)}}{a_{H(0.1)}}$$

which reduces finally to

$$[E_o(1)-E(1)]-[E_o(2)-E(2)]=\frac{RT}{F}\ln\frac{a_{Cl(C+0.1)}}{a_{Cl(0.1)}}$$

Values for $E_o(1)-E(1)$ can be readily obtained from Table I by subtracting the values for each concentration of the three chlorides from the electromotive force value given at the head of the table as concentration 0.00. These values are given in the first part of Table VII.

TABLE VII.

$E_o(1)-E(1)$

c	$BaCl_2$	$SrCl_2$	$CaCl_2$
0.1	0.02368	0.02398	0.02436
0.2	0.03561	0.03580	0.03593
0.3	0.04395	0.04449	0.04572
0.5	0.05743	0.05867	0.05912
0.75	0.07112	0.07268	0.07379
1.00	0.08220	0.08427	0.08618
1.3	0.09540		
	$[E_o(1)-E(1)]-[E_o(2)-E(2)]$		
0.1	0.02228	0.02238	0.02242
0.2	0.03260	0.03243	0.03203
0.3	0.03915	0.03919	0.03973
0.5	0.04861	0.04908	0.04871
0.75	0.05680	0.05737	0.05728
1.00	0.06231	0.06286	0.06308
1.3	0.06882		

The values for $E_o(2)-E(2)$ are those given in Table II. The difference between these two sets of values is shown in the second part of Table VII. The maximum difference for any one concentration is 0.00058 volts and the average difference for the six concentrations given is but .00041 of

a volt. This is very small considering the high concentrations of the solutions. The slight deviation still further substantiates the belief that common ion activities under the same conditions are identical. Harned in his work with the alkaline metal chlorides (loc. cit.) likewise found that the deviation present was well within the probable experimental errors.

d. THE CALCULATION OF THE ACTIVITY COEFFICIENTS OF THE HYDROGEN ION AND THE CHLORINE ION AT 25° IN 0.1M HYDROCHLORIC ACID CONTAINING BARIUM, STRONTIUM AND CALCIUM CHLORIDES AT CONCENTRATIONS UP TO 1. M.

As shown above under the reaction of Independent Activities of Ions

$$[E_o(1)-E(1)]-[E_o(2)-E(2)]=\frac{RT}{F}\ln\frac{a_{Cl(C+0.1)}}{a_{Cl(0.1)}}$$

The values in volts for the first member of the above equation are given in the second part of Table VII. The value for $a_{Cl(0.1)}$ has been determined by Harned (J. A. C. S., 44, 252, 1922), and calculated as .0779. From the same source the value for a_H is derived as 0.0868. Substituting numerical values in the above equation and solving for a_{Cl} there is given

$$\log a_{Cl}=\log .0779+\frac{e.m.F.}{.05915}$$

where the constant .05915 represents the numerical values of $\frac{RT}{F}\times$ logarithmic conversion factor.

In a similar manner the expression for a_H is

$$\log a_H=\log .07638+\frac{e.m.F.}{.05915}$$

The values of e. m. f. for a_{Cl} were obtained from the first part of Table VI and those for a_H from Table II. The values for a_{Cl} and a_H as calculated above are given in Table VIII.

TABLE VIII. PART 1.

Values of $(a_{Cl})_{25°}$

c	$BaCl_2$	$SrCl_2$	$CaCl_2$
0.1	0.18544	0.18617	0.18645
0.2	0.27712	0.27530	0.27105
0.3	0.35760	0.35817	0.35746
0.5	0.51684	0.52638	0.51883
0.75	0.71090	0.72684	0.72414
1.00	0.88097	0.90003	0.90790
1.3	1.13508		

TABLE VIII. PART 2.

Values of (a_H)

c	$BaCl_2$	$SrCl_2$	$CaCl_2$
0.000	0.0868	0.0868	0.0868
0.100	0.0969	0.0974	0.0987
0.200	0.1029	0.1042	0.1064
0.300	0.1102	0.1127	0.1151
0.500	0.1290	0.1332	0.1371
0.750	0.1599	0.1661	0.1735
1.000	0.1984	0.2105	0.2248
1.3	0.2577		

SUMMARY.

1. Measurements of the electromotive forces of the cells

$$H_2 \mid MeCl_2\ (c) \text{ in HCl } (0.1) \mid HgCl \mid Hg$$

at 18°, 25° and 30° containing barium, strontium and calcium chlorides, have been made.

2. Measurements of the cells

$$H_2 \mid MeCl_2\ (c) \text{ in HCl } (0.1) \mid KCl\ (Sat.) \mid HgCl \mid Hg$$

at 25° containing barium, strontium and calcium chlorides, have also been made.

3. Values for the cells

$$H_2 \mid HCl\ (0.1) \mid HgCl \mid Hg$$

and

$$H_2 \mid HCl\ (0.1) \mid KCl\ (Sat.) \mid HgCl \mid Hg$$

at 25° were checked with values of the same cells found by other investigators.

4. The values for the free energies and heat content decreases of the cell reaction

$$H_2 + 2\ HgCl = 2HCl\ (0.1) + 2Hg$$

in the presence of barium, strontium and calcium chlorides, respectively, have been computed.

5. The decrease in free energy and heat content function of transfer of the chlorine and hydrogen ions respectively from $MeCl_2$ (c) in HCl (O. 1M) to HCl (0.1) have been compiled.

6. The independent chloride ion activity in the various salt solutions proposed by MacInnes and found to hold within narrow limits by Harned, has been further substantiated.

7. The activities of the hydrogen ion and the chlorine ion at 25° in 0.1M hydrochloric acid containing barium, strontium and calcium chlorides at concentrations up to 1.M have been found.